functions which rise rapidly and then fall off, it seems altogether likely that Smith's many critical potentials may be explained in this way.

Summary and Conclusions

1. It has been demonstrated that it is possible to build an apparatus for the determination of the electronic excitation and ionization functions of mercury, which is sufficiently free from spurious effects to permit the accurate determination of the energy of the bombarding electrons from the dimensions of the apparatus and the strength of the magnetic field.
2. Measurements of the photoelectric current, emitted from an electrode within the region of excitation, show that the probability of exciting the $2^3P_1{}^0$ level of the mercury atom rises rapidly from zero at 4.9 volts to a maximum at 5.6 volts and that the excitation of the $3^3P_1{}^0$ and the $4^3P_1{}^0$ levels are characterized by similar curves with maxima at 8.9 and 9.6 volts, respectively.
3. Ionization has been observed to set in at 10.4 volts and rise to a distinct maximum at 10.8 volts followed by a minimum at 11.05 volts. Definite structural details of a minor character were observed up to about 16 volts.
4. The *efficiency* of ionization has a maximum of 19.2 ionic charges per electron per cm path at 1 mm pressure and 0°C for an electron energy of 42 volts while the *probability* of ionization to the first stage has a maximum of 18.2 at 32 volts.

It is a pleasure to acknowledge my indebtedness to my colleagues at the Institute and in particular to Dr. Arthur R. von Hippel for the opportunity of discussing with them many of the interesting problems which arose in connection with this research. For technical assistance I am indebted to Mr. Allyn B. White and for the skillful glass-blowing required in the preparation of the experimental tube I owe much to Mr. Lawrence W. Ryan.

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Spark Breakdown Potentials as a Function of the Product of the Pressure by the Plate Separation in A, N_2 and H_2 for Pt and Na Cathodes

Florence Ehrenkranz
University of California, Berkeley, California

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Measurements were made on the sparking potentials between fixed plane parallel electrodes in purified, *mercury-free* A, N_2 and H_2 for Pt and Na cathodes for extended pressure ranges. The effect on the sparking potentials in H_2 produced by heated Pt and Na cathodes was investigated. In all of the gases studied, the values of the sparking potential are lower for a Na-coated Pt cathode than for a clean Pt cathode throughout the pressure ranges investigated. The percentage lowering, which is especially pronounced near the minimum sparking potential, decreases with increasing $p\delta$. In A, the sparking potentials for a Pt cathode agree very closely with the Fe cathode values of Penning except in the vicinity of the minimum sparking potential; the discrepancy at low values of $p\delta$ is caused by the difference in cathode surface. For a Na-coated surface, the sparking potentials are 50 percent lower in the vicinity of the minimum and 7.5 percent lower at $p\delta$ equal to 240 mm×cm. The predischarge currents within a few volts of breakdown were less than 10^{-9} amp. for both Na and Pt surfaces. The effect of a Na cathode on the breakdown potentials in A is in satisfactory agreement with the quantitative predictions of classical Townsend theory given by Loeb. In N_2, the lowering produced by Na is 28 percent near the minimum and 20 percent at $p\delta$ equal to 340 mm×cm. The N_2 results are not applicable to the theory discussed by Loeb because of the heavy predischarge currents, 360 microamperes at $p\delta$ equal to 356, which occur in the presence of Na. The lowered sparking potentials and the heavy predischarge currents, as well as the increase in the values of the Townsend coefficient α in the presence of a Na-covered cathode which was observed by Bowls, indicate that there occurs in the presence of Na a volatile substance, Na or something else, of vapor pressure greater than 10^{-4} mm and ionization potential less than that of N_2 which acts independently of cathode phenomena. H_2 is intermediate between N_2 and A both with respect to the approach of the Na and Pt curves at high $p\delta$ and the magnitudes of the predischarge currents. In the H_2-Na case, the marked predischarge currents and the lowered sparking potentials are probably caused by a volatile impurity, Na or something else. The sparking potentials in H_2 with heated Pt and Na cathodes are identical within the limits of experimental error. The coincidence at both low and high values of $p\delta$ may be explained by the formation of NaH and the distilling off from the heated surface of the Na and/or NaH. At low values of $p\delta$, the sparking potentials are governed considerably more by cathode phenomena than by the primary process of ionization by collision. The *heated* Na cathode has no Na nor NaH deposited on it; the cathode emission properties are the same therefore as those of the heated Pt surface. Hence, the sparking potentials are the same. At high values of $p\delta$, α is predominant in determining the sparking potentials, and α is very sensitive to the presence of Na. The formation of NaH, which occurs because of the presence of the heated cathode, probably removes most of the Na vapor and destroys all of the volatile substance which causes the lowering in the case of the cold Na cathodes.

INTRODUCTION

NUMEROUS investigations,[1–3] of which those of Paschen[4] in 1889 were among the earliest, on sparking potentials as a function of the product of the pressure by the plate separation $p\delta$ have established the general form of curve which obtains for all gases. This well-known curve has a minimum at some value of $p\delta$, between 0.5 and 4 mm Hg·cm for most gases. Recently, Penning[5–7] and his associates have shown that very small traces of mercury vapor, for example 10^{-4} percent, greatly lower the values of the sparking potential as a function of $p\delta$ in the inert gases, neon and argon. No measurements of sparking potentials in a mercury-free *molecular* gas have been reported. Further, no investigation with modern technique on the effect of *cathode material* on the breakdown potentials *over an extended pressure range* has been made. Loeb[8] has shown that classical Townsend theory predicts a marked cathode effect at low pressures and a small cathode effect at high pressures.

It was the purpose of this investigation to determine the sparking potentials between fixed, plane parallel electrodes, with Pt and Na-coated Pt cathodes, in purified, mercury-free N_2, H_2, and A for extended pressure ranges. Measurements were made for $p\delta$ equal to and greater than the $p\delta$ which corresponds to the minimum sparking potential. Pt and Na-coated Pt surfaces were used because it was anticipated that a cathode effect would be especially marked for these metals because of the large difference in work functions. N_2 was used for the molecular gas because it was hoped that a correlation could be made between the sparking potential data and Bowls'[9] data on the Townsend coefficients in mercury-free N_2. The unexpected results of Bowls on the Townsend coefficients and the

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[1] J. J. Thomson, *Conduction of Electricity through Gases* (1903), p. 352.

[2] W. O. Schumann, *Elektrische Durbruchfeldstärke von Gasen* (1923), pp. 94, 95, 96.

[3] Engel and Steenbeck, *Elektrische Gasentladungen*, Vol. 2 (1934), p. 335.

[4] J. S. Townsend, *Electricity in Gases* (1916), p. 351.

[5] F. M. Penning, Naturwiss. **15**, 818 (1927).

[6] F. M. Penning, Zeits. f. Physik **46**, 341 (1928); **57**, 723 (1929); **72**, 338 (1931).

[7] Penning and Addink, Physica **1**, 1007 (1934).

[8] L. B. Loeb, Rev. Mod. Phys. **8**, 267 (1936).

[9] W. E. Bowls, Phys. Rev. **53**, 293 (1938); Thesis (University of California Pub.) 1938.

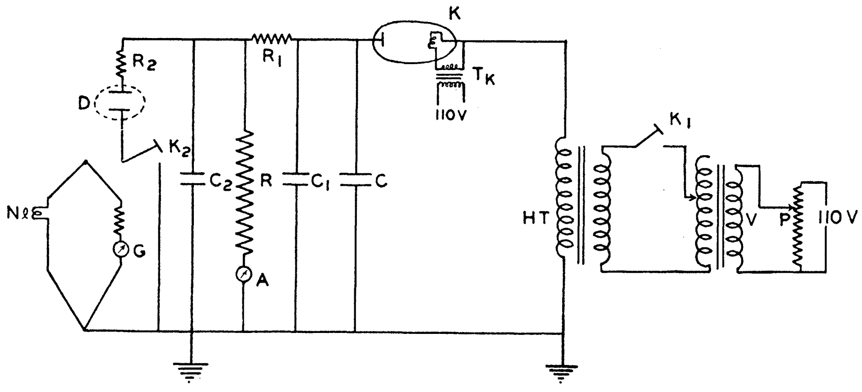

FIG. 1. Diagram of electrical circuit.

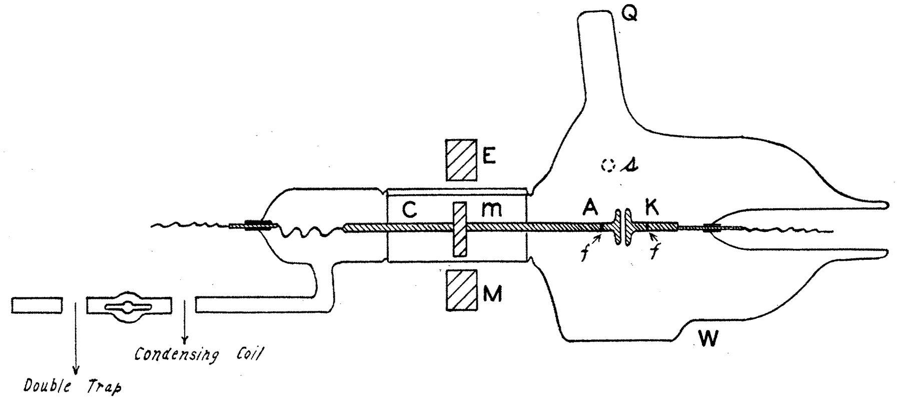

FIG. 2. Horizontal cross section of the discharge tube.

author on the sparking potentials for N_2 in the presence of a Na surface indicated that it would be very desirable to investigate a mercury-free molecular gas which is not characterized by metastable and active states. The second molecular gas chosen, therefore, was H_2. Argon was investigated because data obtained by Neuman,[10] several years ago, indicated that the sparking potentials in A for cold Ni and Na surfaces were identical for pressures greater than 20 mm; for lower pressures, the breakdown potentials were the same for a *heated* Na surface and a cold Ni cathode. It was of interest to see whether these results could be confirmed.

APPARATUS AND EXPERIMENTAL PROCEDURE

The electrical circuit is shown in Fig. 1. Filtered, half-wave rectified voltage is impressed on the plane-parallel electrodes of the discharge tube, *D*, by the various devices indicated. Sparking potential measurements were made by throwing the switch K_2 to the right and observing the deflection in the current-reading instrument, *A*, as the voltage across the gap was increased slowly by manipulating the hand-operated variac, *V*. At breakdown the needle of *A* dips abruptly and the sparking potential is calculated from the current just before the breakdown and the resistance, *R*. Voltages above 750 volts are accurate to within 1.5 percent; voltages below 750 are accurate to within 2.5 percent except for voltages below 250, where the accuracy may be somewhat less.

Predischarge currents within a few volts of breakdown were measured by closing K_2 to the left and observing the reading of the galvanometer, *G*, just before the spark breaks.

A horizontal cross section of the discharge tube is shown in Fig. 2. The cathode, *K*, was 36 mm in diameter; the anode was slightly smaller. Both electrodes had curved edges; the curvature was such that flat portions were opposite. The cathode, which was fixed, consisted of 0.008-inch Pt sheet spun over a Ni plate; the anode was made of 0.118-inch Ni. The anode could be moved to any desired plate separation by the action of a double-pole electromagnet, *EM*. Various plate separations between 0.55 and 0.80 cm were used. For any one series of measurements, the plates were separated by a fixed distance and the pressure varied. The separation was measured by a comparator through the Pyrex window, *W*. The accuracy of this measurement is of the order of 1 percent.

Light could be focused on *K* through the quartz window, *Q*. A quartz mercury arc was used with the Pt cathode and a Mazda lamp with the Na surface. The side arm, *s*, contained a Na capsule. The capsule could be broken in vacuum. The Na in the capsule was purified by repeated vacuum distillation. The electrodes and the bulb itself were cleaned with acid, grain alcohol and distilled water.

The discharge tube was connected to the pressure gauges, the gas supply and the pumping system through a stopcock on each side of which was a liquid-air trap. The trap between the stopcock and the tube was a helical Pyrex coil

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[10] L. J. Neuman, Proc. Nat. Acad. Sci. **15**, 259 (1929).

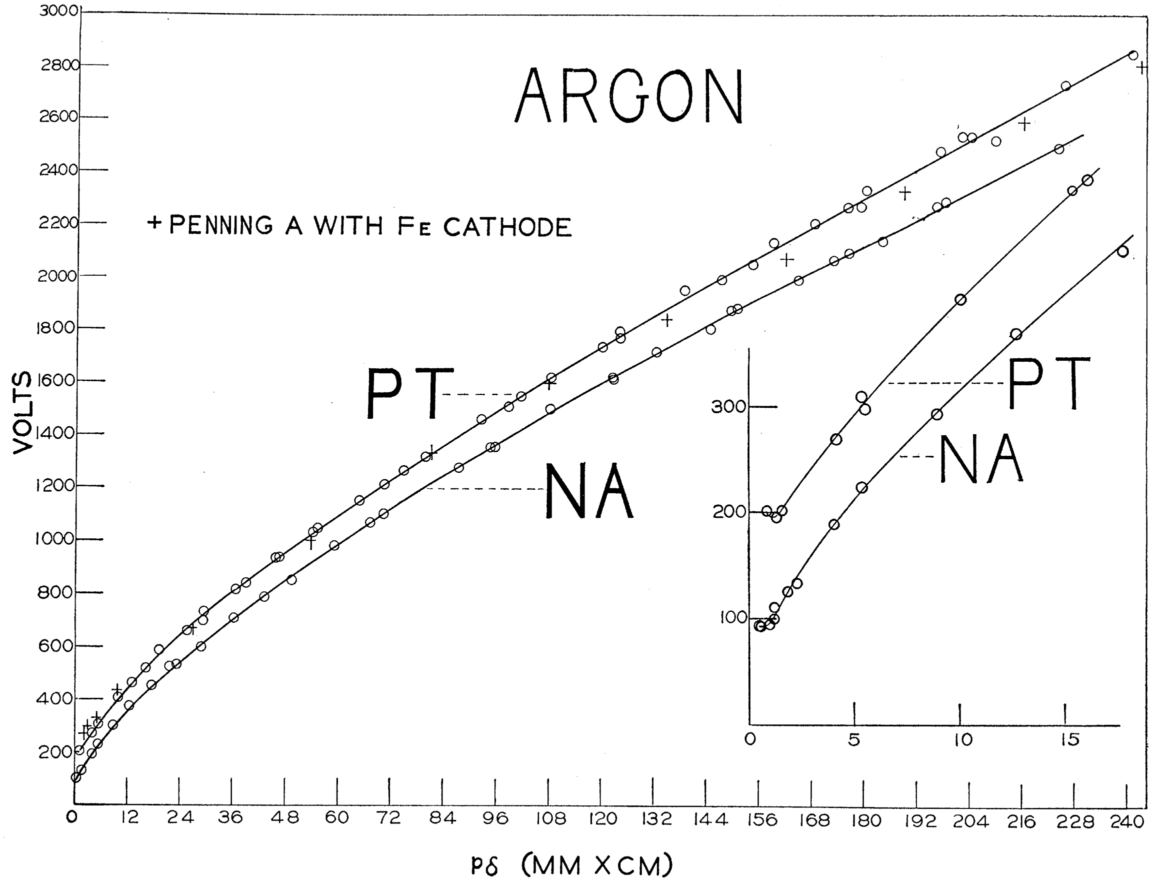

FIG. 3. The sparking potential as a function of pressure×plate separation for Pt and Na cathodes.

with an effective length of 43 cm. For each run made with the Pt cathode, the tube was outgassed at 490°C for one hour. All of the glass tubing between the gas reservoir and the tube was heated with a Bunsen flame during the outgassing of the tube. The stopcock was open only when the double liquid-air trap on the far side of the tube from the stopcock was immersed in liquid air. Before starting a run, a glow discharge was maintained between the plates for about one hour in a few millimeters of purified gas; this gas was pumped out and the tube flushed again with purified gas. Then gas was admitted to the tube at the beginning of the run to the highest pressure to be used in that series of measurements. Thus the usual procedure was to take a measurement at the highest pressure, pump gas from the tube, take another measurement and repeat until the minimum sparking potential was reached.

The procedure for the Na cathode experiments was as follows: The tube was outgassed at 490°C and allowed to cool. With the pumps still working, the Na capsule was broken and the Na distilled on the electrodes. After the Na had cooled, the tube was flushed with purified gas. For the next run, the Na was redistilled by heating the tube with a Bunsen flame. Liquid air was kept on the condensing coil continuously from the time the tube was outgassed until the last Na run for that tube was made. After taking two or three sets of measurements with a given Na surface, the tube and all its elements were dismantled and cleaned; then the tube was reassembled and a side arm containing a fresh Na capsule added.

Pressures were measured by a closed mercury manometer and a McLeod gauge. The accuracy of the pressure measurements was 1 percent or better except for the lowest pressures. For

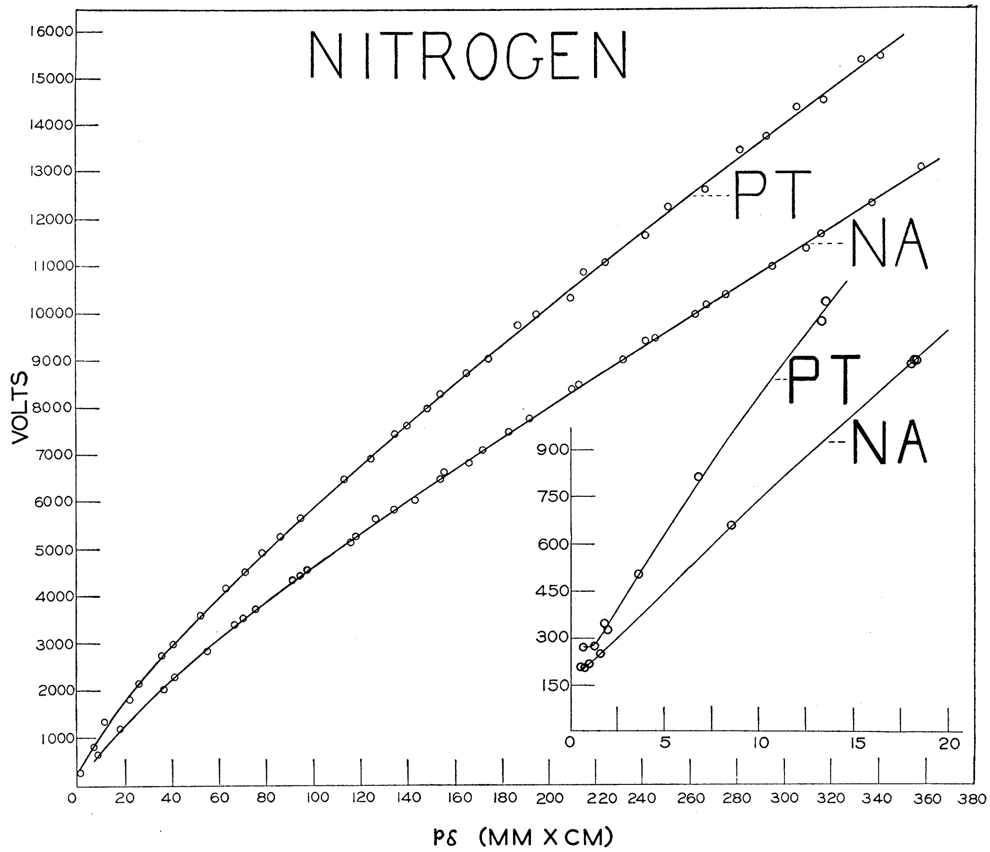

FIG. 4. The sparking potential as a function of pressure×plate separation for Pt and Na cathodes.

pressures less than 3 mm, the error may be greater than 1 percent. The pressures are given as read at the room temperature of 22°C.

PURIFICATION OF THE GASES, TESTS FOR PURITY, PREDISCHARGE CURRENTS

Commercial A was passed over a drying train and then was purified at a pressure of 55 cm in a Ca arc run on 220 d.c. at about 11 amperes for 110 hours. Commercial N_2 was purified by admitting gas very slowly over liquid air to a tube containing heated Cu and CuO filings. The gas then passed through a drying train and circulated in a tube containing a glowing tungsten filament. Electrolytic H_2 was used for most of the H_2 runs; for a few series of measurements, a palladium tube was employed.

The purity of the gases was investigated spectroscopically. Spectrograms in the ultraviolet region of a glow discharge maintained between the discharge plates were obtained by focusing a Hilger quartz spectrograph on the cathode. The sparking potential values given in Fig. 3 for A correspond to runs for which the spectroscopic tests showed no Hg and no bands. The values for N_2 for a Pt cathode given in Fig. 4 correspond to runs for which the spectrograms in the ultraviolet region showed N_2 bands only. *Series for which the spectrograms showed the resonance* Hg *line 2536*A *and/or* NO *bands, however weak, gave sparking potential values between 7 percent and 13 percent lower than those for pure* N_2. The ultraviolet spectrograms for H_2 with a cold Pt cathode always showed a weak OH band as an impurity. This is almost certainly formed from hydrogen and oxygen released from the electrode surface under the discharge conditions. The effect of spectroscopic traces of N_2 was to raise the sparking potential values by a small percentage above the values given. Spectroscopic traces of CO which occurred in one series of measurements appeared not to affect the sparking potential. The spectrograms for H_2 with a heated cathode (Pt or Na) showed traces of N_2, OH, CO.

Predischarge currents within a few volts of breakdown in A with a Pt cathode were less than 10^{-9} ampere except for $p\delta$ less than 30 mm·cm. For the low values of $p\delta$ currents of the order of 10^{-7} ampere occurred when the cathode was illuminated with ultraviolet light. The currents fell to less than 10^{-9} ampere when the radiation was cut off. For A with a Na cathode, the currents were less than 10^{-9} ampere. Predischarge currents for *pure* N_2 with a Pt cathode were less than 10^{-9} ampere. In N_2 contaminated with spectroscopic traces of Hg, peculiar current fluctuations occurred. Thus four successive current measurements at a given $p\delta$ were: 2 microamperes, 3 microamperes, 2×10^{-9} ampere, 1 microampere. For N_2 with a Na cathode, marked predischarge currents ranging from 360 microamperes at a $p\delta$ of 356 to 10 microamperes at a $p\delta$ of 2 occurred. A noteworthy feature with N_2-Na was that the first spark at a $p\delta$ of 356, say, would yield a predischarge current of 230 microamperes; with the passage of a few sparks, the current would increase until a reproducible value of 360 microamperes was reached. Predischarge currents for H_2 with a Pt cathode were less than 10^{-9} ampere. For H_2-Na, the currents ranged from 8 microamperes at a $p\delta$ of 350 to 1 microampere at a $p\delta$ of 10.

Experimental Results and Discussion

The experimental values of the sparking potential are given in the curves of Figs. 3, 4, 6 and 7. In A, the sparking potential values cover a pressure range of 0.5 to 400 mm of Hg. The Pt values agree very closely with Penning's[7] iron cathode values, corrected to 22°C, except in the vicinity of the minimum. The difference there is due to the difference in *cathode surface*. This is confirmed by the experimental observation that the minimum value for Pt is gradually increased from 200 to 275 volts on bombardment of the electrodes for several hours by means of a high frequency discharge maintained between the plates.

The lowering produced by Na is 50 percent at the minimum breakdown potential. The percentage lowering, which decreases with increasing $p\delta$, is 7.5 percent at $p\delta$ equal to 240 mm·cm. The lowering at low $p\delta$ conforms to observations on other pure gases.[11–14] The

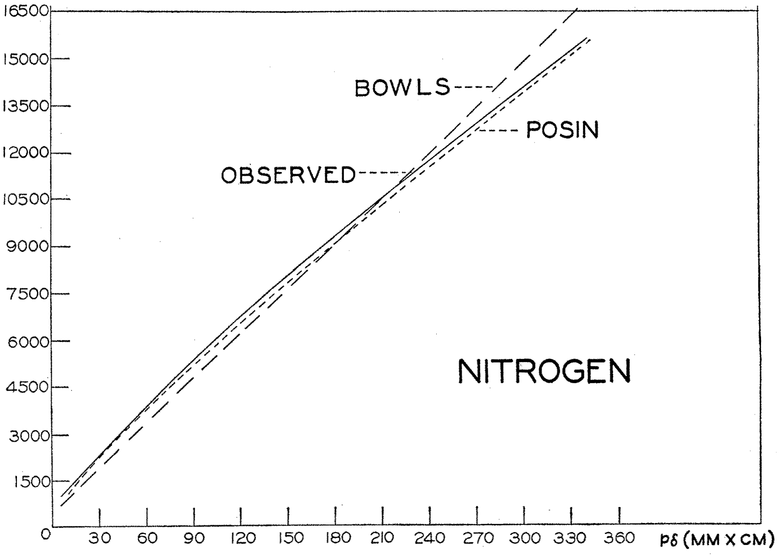

FIG. 5. Calculated sparking potential curves *vs.* the experimental curve for $10<p\delta<360$.

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[11] Holst and Oosterhuis, Versl. Kon. Akad. van Wet. Amsterdam **29**, 849 (1920).

[12] Holst and Oosterhuis, Comptes rendus **175**, 577 (1922).

[13] James Taylor, Proc. Roy. Soc. **A114**, 73 (1927); **A117**, 508 (1928).

[14] Engel and Steenbeck, reference 1, p. 46.

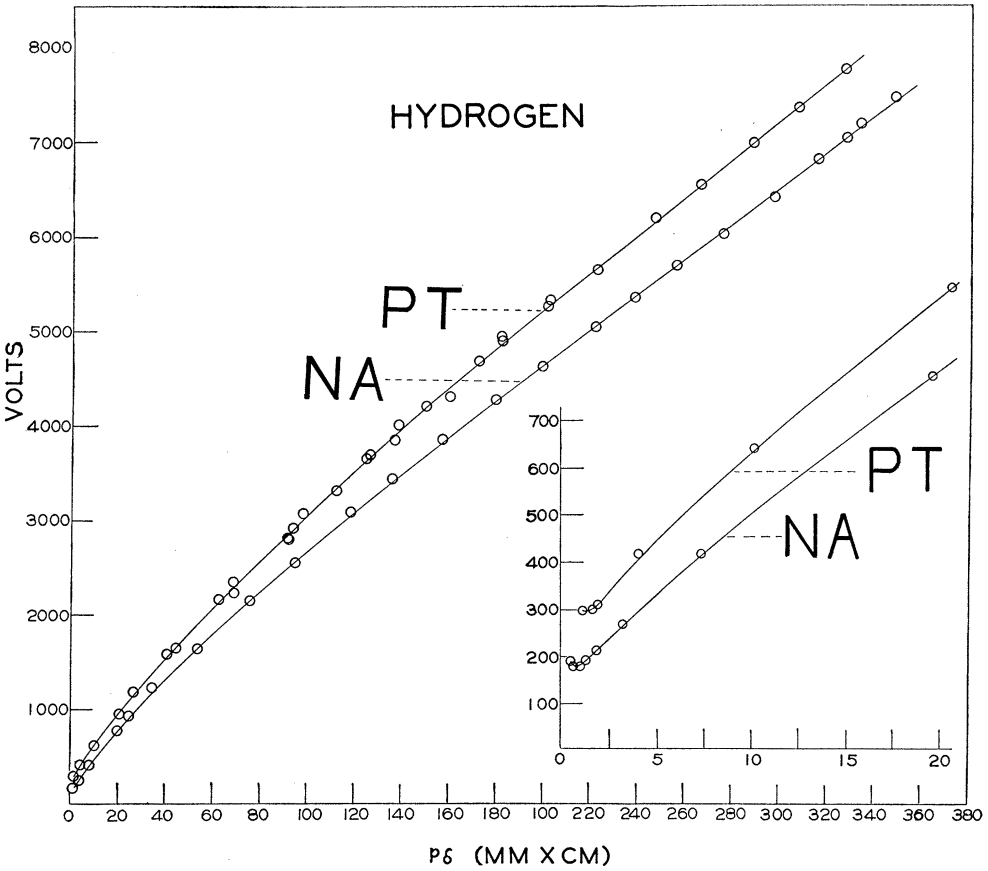

FIG. 6. The sparking potential as a function of pressure×plate separation for Pt and Na cathodes.

sparking potential values at high $p\delta$ do not become as nearly equal for the two cathodes as the simple hypotheses given in Loeb's[8] paper anticipate; nevertheless, the agreement between theory and experiment is satisfactory.

In N_2, the sparking potential values correspond to a pressure range of about 0.5 to 600 mm of Hg. The lowering produced by Na near the minimum is 28 percent and at $p\delta$ equal to 240 mm·cm, it is 20 percent. Thus, the results in N_2 appear to be highly anomalous with respect to theory since the 20 percent lowering produced in the presence of a Na cathode at high $p\delta$ is beyond its predictions. The discrepancy is probably to be associated with the heavy predischarge currents, since the theory does not consider the effect of such currents.

The inferences which may be drawn from the N_2-Na experiments are as follows.

(1) The lowering of the sparking potentials is in qualitative agreement with the increase in the Townsend coefficient, α, in the presence of Na observed by Bowls.[9]

(2) Both Bowls' results on an increased α and the author's results on high predischarge currents and lowered sparking potentials suggest that there occurs in the presence of Na a volatile substance which has a vapor pressure greater than 10^{-4} mm, an ionization potential less than that of N_2, and that it acts independently of cathode phenomena. That this vapor was not hydrogen, as suggested by Bradbury,[9] was proved by the deliberate introduction of various concentrations of hydrogen between 0.03 percent and 11 percent; the sparking potentials for the admixtures with a Pt cathode differed from those for pure N_2 by less than 2 percent. That the very low vapor pressure of Na at room temperature, 10^{-10} mm of Hg, cannot of itself account for his increase in α was shown by Bowls.

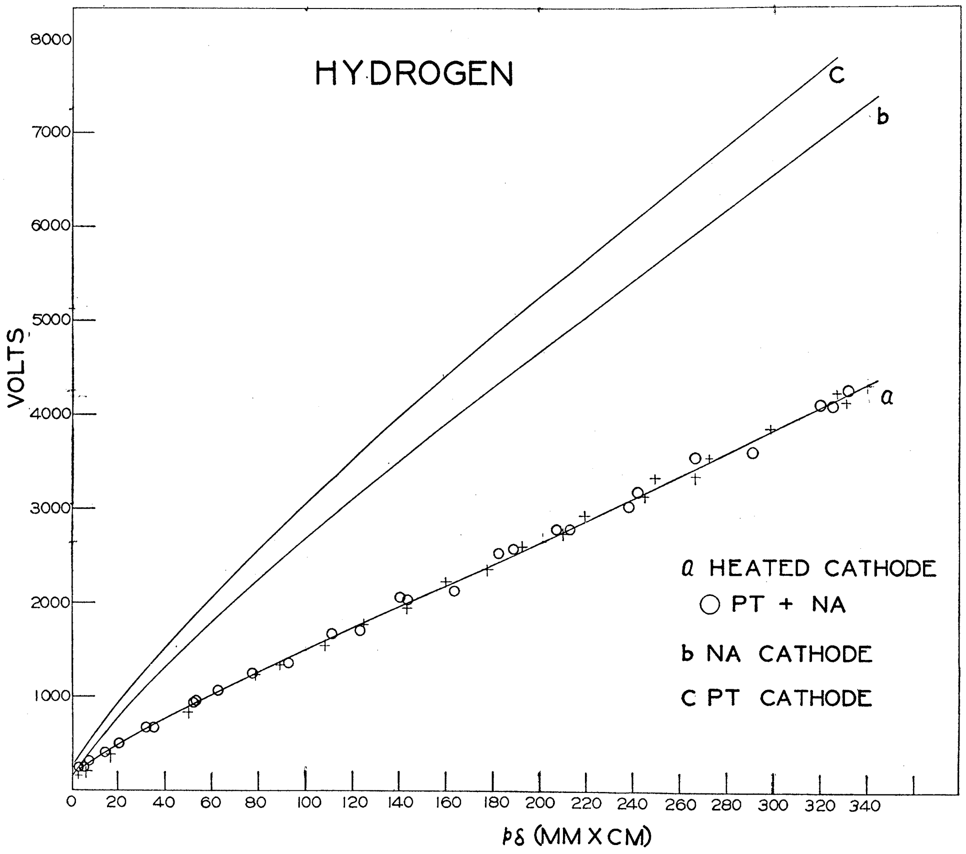

FIG. 7. The sparking potential as a function of pressure×plate separation for heated Pt and Na cathodes.

(3) Under the conditions of discharge in the present work, the Na vapor pressure may have been much greater than 10^{-10} mm of Hg; consequently, it is possible that the lowered sparking potentials are caused by ionization of Na atoms in the gap by metastable N_2 molecules of 8.2 volts energy and by electrons. At present, there is no definite evidence as to the character of the volatile substance. If it is Na, there is no completely satisfactory explanation of its exaggerated vapor pressure in Bowls' experimental chamber since he did not have discharge conditions and his gas-intensified photoelectric currents were very small, about 10^{-13} ampere.

An attempt was made to correlate the author's data for Pt with Bowls' data on the Townsend coefficients in mercury-free N_2.[15] The results of these calculations for a Pt cathode for $p\delta$ greater than 15 mm·cm are shown in Fig. 5. In the broken curve, values of V for $p\delta$ greater than 60 are extrapolated values from Bowls' data. It is seen that although Bowls' data are applicable, to these results, satisfactory agreement does not obtain between the Townsend coefficient data and the sparking potential data. This may, in part, be attributed to the lack of adequate data in Bowls' experiments at low X/p.

The dotted curve of Fig. 5 represents Posin's[16] values for the sparking potentials in N_2 computed from Townsend coefficients for *mercury-contaminated* N_2. In view of the observed lowering of the sparking potentials in the presence of mercury, it appears very probably that the agree-

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[15] For the procedure used in making these calculations, see Loeb's paper, reference 8, pp. 276–7. In the present case, the empirical relation used was $\alpha/p = 0.6 \ln X/p - 2.32$; X/p is the ratio of the field strength in volts per cm to the pressure in mm of Hg. This relation fits Bowls' data for an X/p range between 94 and 59; the corresponding $p\delta$ range is between 15 and 100.

[16] D. Q. Posin, Phys. Rev. **50**, 650 (1936).

ment between Posin's data and the author's data is fortuitous.

The breakdown potentials in H_2, for Pt and Na surfaces, are given in Fig. 6. The corresponding pressure range is from about 0.5 to 570 mm of Hg. The lowering produced by the presence of Na is 30 percent near the minimum sparking potential and at a $p\delta$ of 320 mm·cm, it is 11 percent. The marked predischarge currents in the presence of Na suggest that even in H_2 there occurs a volatile substance of low ionization potential which at high $p\delta$ lowers the sparking potentials independently of the action of cathode mechanisms.*

In connection with the H_2-Na measurement the following experimental observation was made. As a result of one or two runs with a Na surface a considerable amount of the Na on the cathode was changed to NaH. The new cathode material is recognizable by its grey color and the heating required for its distillation. Under these circumstances the sparking potentials with NaH present were only 4 percent lower than for a Pt surface except near the minimum where the lowering was 25 percent.

It appears as if the production of NaH had removed some of the volatile Na compound. Finally breakdown voltages in H_2 in the presence of heated cathodes were studied. The procedure in the heated cathode experiments was to heat the cathode to about 600°C. This distilled Na off the cathode and into the gap, and presumably gave Na vapor but a Pt cathode.

It was hoped that such a procedure might indicate whether the lowering of the sparking potential in H_2 in the presence of Na was caused by Na vapor in the gap or to Na actually deposited on the cathode. A definite answer would be given by this experiment only if no chemical reaction occurred between the heated Na and gas. This procedure did not exactly duplicate the conditions under which Neuman had observed that the difference in sparking potential in argon in the presence of Na vapor for cold and hot wire cathodes was the same above 20 mm. In the first place, the hot wire cathode used by Neuman apparently heated the *gas* relatively little compared to the large cathode used here. In these experiments the heated cathode reduced the gas density in the discharge path to about half. It was, therefore, only possible to compare runs made with a heated Pt cathode and a heated Na surface. Secondly, Neuman's results were not complicated by chemical reaction between the gas and Na, since he used A while in this experiment, one dealt with heated H_2 in the presence of heated Na.

The results for H_2 in the presence of heated cathodes are shown in curve *a* of Fig. 7. (Curves *b* and *c* represent control measurements with cold cathodes. The decreased gas density in the heated spark gap lowers the sparking potentials and shifts the minimum to higher values of $p\delta$.) The data plotted in curve *a* show that, within the limits of experimental error, the sparking potential values for a heated Pt cathode are identical with those for a heated Na cathode. One cannot, however, conclude from this that the Na in the gap did not change the sparking potential for it is probable that the formation of NaH removed most of the Na and destroyed all of the volatile substance which causes the lowering in the case of the cold Na cathode. The correctness of this explanation is confirmed by the fact that the operating temperature of the cathode, 600°C with an average gap temperature of 300° was sufficiently high to permit the formation of NaH, which occurs at 350°C, and to evaporate it off the cathode.[17, 18]

The author wishes to express her thanks and appreciation to Professor L. B. Loeb at whose suggestion the problem was undertaken and under whose direction it was carried out. In addition, the author wishes to acknowledge her indebtedness to Mr. William R. Stamper and Mr. E. H. Guyon for their assistance in the frequent dismantling and assemblage of the tube.

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* *Note added in proof:* It has been possible to compare these data in H_2 with direct measurements in H_2 and with curves computed from Hale's values of α and γ in H_2 for Pt and for Pt coated with NaH between $p\delta = 1$ and $p\delta = 30$. In pure H_2 with Pt cathodes Hale's computed and observed values except at the minimum lie about 4 percent *above* the curves of Ehrenkranz. This was possibly due to small traces of impurity in Ehrenkranz's gas as a result of repeated sparking. In Hale's work only single values of the potential were taken for each filling. In the case of the NaH cathode the three curves coincide within the limits of experimental error except near the minimum.

[17] *Handbuch der Anorganische Chemie 11.* Vol. 1 (1908), p. 219.

[18] F. G. Keyes, J. Am. Chem. Soc. **34**, 779 (1912).